

Page 17, lines 11-13, delete current paragraph and insert therefor:

b2
Next, the characteristics of the photomask blank 1 in terms of manufacturing, and the effect thereof as a photomask blank 1, will be described.

Page 17, lines 14-17, delete current paragraph and insert therefor:

b3
Figures 3 and 4 are schematic cross sections illustrating the methods for manufacturing the photomask blank 1 of Example 1 and the photomask 11 of Example 1, respectively.

Page 18, lines 9-18, delete current paragraph and insert therefor:

b4
Quartz glass that absorbs little light with wavelength in the ultraviolet region, as is the case with the exposure light, is particularly good as the transparent substrate 2, but quartz glass generally results in more film stress than soda lime glass or aluminoborosilicate glass, which is thought to be due to different crystal seeds or differences in the coefficient of thermal expansion with a chromium film. Therefore, the present invention is suited to combination with a quartz glass substrate which is suitable as a glass substrate for a photomask.

Page 18, line 19 to page 19, line 6, delete current paragraph and insert therefor:

b5
Then, a CrC film with a thickness of 600 Å was formed as the second shading film (light-shielding film, opaque film, non-transmitting film) 4 as shown in Figure 3 (b) by reactive sputtering using a chromium target in a mixed gas atmosphere composed of argon methane and helium (Ar: 30 vol%, CH₄: 10 vol%, He 60 vol%, pressure 0.3 Pa, sputtering power: 1650 W, deposition rate: 3.4 nm/sec). The carbon content in the CrC film of the above photomask blank 1 was measured and found to be 6 at%, and the etching rate was 0.3 nm/sec. The crystal grain diameter of the CrC film was measured by transmission electron microscope (TEM) and found to be 1 to 7 nm.

Page 19, lines 7-14, delete current paragraph and insert therefor:

b6
The method of the present invention for manufacturing a photomask blank 1 solves the problems mentioned above by having the helium serving as the inert gas be contained as a type of mixed gas. Figure 3 (b) here shows an example in which the helium content in the mixed gas is 60 vol%, but the proportions in which the gases are mixed in this mixed will be discussed in detail below on the basis of experimental results.

Page 19, line 23 to page 20, line 7, delete current paragraph and insert therefor:

b7
The oxygen and nitrogen contents in the CrON film of the above photomask blank 1 were measured and found to be 45 at% oxygen and 25 at% nitrogen. The optical characteristics of the photomask blank 1 produced in this manner were measured using a commercially available apparatus, and at a wavelength of 365 nm, the optical density was 3.0 and the surface reflectance was 12%. There were no defects in any of the films, meaning that the film quality was good.

Page 20, lines 9-12, delete current paragraph and insert therefor:

b8
The sheet resistance was measured for the photomask blank 1 of CrN/CrC/CrON films finally obtained, whereupon the conductivity was good, being 25 ohms per square or less. This indicates that charges tend not to build up between the CrON film and the resist during electron exposure.

Page 20, line 18 to page 21, line 9, delete current paragraph and insert therefor:

b9
The specific heating method used for this analysis involved guiding the light from an infrared lamp outside the vacuum system into a measurement chamber through a rod of molten quartz, which is highly transparent, and placing a sample holder made of the above-mentioned opaque quartz on the upper end of the rod. A sample cut out in a size of 10 mm² from the photomask blank 1 obtained above is placed on the opaque quartz sample holder of the thermal desorption gas analyzer, and the sample is heated by infrared rays from below.

B9
Cald

The sample temperature is measured by a thermocouple in contact with the thin film surface. Here, the degree of vacuum was approximately 4×10^{-7} Pa and the temperature elevation rate was 10 to 60°C/min, and the measurement was made with a mass spectrometer for the gas desorption behavior of mass number (m/e) = 4 (He) when the room temperature was varied up to approximately 850°C.

Page 22, lines 12-22, delete current paragraph and insert therefor:

B10

Thus, if helium is contained as a mixed gas in sputtering in the formation of the chromium carbide film, the diameter of the grains forming the CrC will be small (1 to 7 nm), a good thin film with no film stress will be obtained, and a photomask blank 1 with little change in flatness will be obtained. The mechanism of this is not certain, but is surmised to be that while the crystals of the CrC film become fine, they are not amorphous, and the admixture of helium (He) atoms that do not participate in the bonding of the chromium grains hinders the crystal growth of the chromium while the CrC is being formed.

Page 22, line 23 to page 23, line 8, delete current paragraph and insert therefor:

B11

As shown in Figures 4 (a), a resist 6 was applied by coating over the CrON film serving as the anti-reflective film 5, and this was subjected to pattern exposure and developing to form a resist pattern as shown in Figure 4 (b). CrON not only has an anti-reflective function, but also has an anti-oxidizing function, and consequently its durability is good and it exhibits good characteristics for a photomask blank 1. Thus, adhesion is good with the resist used in a subsequent step, and the above-mentioned patterning can be carried out stably and to high precision.

Page 25, lines 9-17, delete current paragraph and insert therefor:

B12

Even when the helium content in the mixed gas was about 40 vol%, a good film could be obtained by adjusting the sputtering power. When the helium content in the mixed gas was lowered to about 30 vol%, the change in flatness was approximately -1.8 μm , but the

b12
positional precision of the mask pattern in the photomask 11 produced using this photomask blank 1 was within a range that can be identified as passable. In terms of the positional precision of the mask pattern, it is preferable for the change in flatness to be $-2\text{ }\mu\text{m}$ or less.

Page 25, line 23 to page 26, line 15, delete current paragraph and insert therefor:

b13
Although not shown in the graph, a photomask blank 1 was produced by further lowering the sputtering power and setting the thin film deposition rate to 0.5 nm/sec , but no film stress that would pose a problem was generated, and the photomask blank 1, as well as the photomask 11 produced using this blank, underwent little change in flatness and has good pattern positional precision, within the passable range. Conversely, when a photomask blank 1 was produced by raising the sputtering power and setting the thin film deposition rate to approximately 6 nm/sec , no particles that would pose any particular problem were observed in the thin film, and the photomask blank 1, as well as the photomask 11 produced using this blank, were within the passable range. The sputtering gas pressure here was 0.2 to 0.6 Pa , and the sputtering power was 950 to 3000 W . Preferably, due to the relationship with the film stress and film defects, the sputtering power should be 1200 to 2000 W .

Page 26, line 16 to page 27, line 7, delete current paragraph and insert therefor:

b14
 $m/e = 4$ (helium) desorption was observed with a thermal desorption gas analyzer, and it was shown that the films contained helium in the photomask blank 1 of Example 1 produced under the above sputtering conditions, but when the helium gas content in the mixed gas was varied to 80 vol\% , 60 vol\% , and 40 vol\% and the $m/e = 4$ relative intensity (helium) was confirmed to increase in proportion to the helium content in the mixed gas. This tells us that the amount of helium contained in a film obtained by sputtering can be adjusted by adjusting the helium content in the mixed gas. The above-mentioned relative intensity is the quotient of dividing the integral intensity ratio in the pyrogram Figure 7 by the sample surface area ratio (in this case, the relative intensity was set at 1 when the helium gas

B14 content was 80 vol%).

Page 27, lines 8-21, delete current paragraph and insert therefor:

B15
Thus, at least when forming the CrC film, film stress can be suppressed by introducing helium gas into the atmosphere gas, and a photomask blank 1 with good film quality can be obtained while ensuring a high yield, without any adverse effect of impurities from the target. Also, no particular film stress occurred when the CrC film was formed in a thickness of approximately 250 to 1100 Å and the CrON film in a thickness of approximately 200 to 300 Å, and it was possible to obtain a good photomask blank 1, as well as a good photomask 11 using this blank. It is also possible to suppress film stress by introducing helium gas during the formation of not only the CrC film but also the CrON film. A photomask blank 1 having even better film quality is obtained in this case.

Page 30, lines 7-22, delete current paragraph and insert therefor:

B16
With the photomask blank 31 pertaining to the example shown in Figure 8, a quartz glass substrate measuring 5 inches × 5 inches × 0.09 inch and whose main surface and end faces had undergone precision polishing was used as the transparent substrate 12. Over this transparent substrate 12 were formed the first shading film (light-shielding film, opaque film, non-transmitting film) 13 composed of chromium nitride film containing chromium and nitride (film thickness: 150 Å), a second shading film (light-shielding film, opaque film, non-transmitting film) 14 composed of a chromium carbide film containing chromium and carbide (film thickness 600 Å), and an anti-reflective film 15 composed of a chromium oxynitride film containing chromium, oxygen, and nitrogen (film thickness: 250 Å). The photomask 32 shown in Figure 9 was patterned by etching the photomask blank of Figure 8.

Page 30, line 23 to page 31, line 13, delete current paragraph and insert therefor:

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Next, the methods for manufacturing the photomask blank 31 and photomask 32 of the present invention in Example 2 will be described. The transparent substrates 12

B17

composed of quartz glass and measuring 5 inches \times 5 inches \times 0.09 inch and whose main surface and end faces have undergone precision polishing are put on a substrate holder (pallet) and introduced into the inline continuous sputtering apparatus shown in Figure 6. In the simplest terms, this inline sputtering apparatus consists of three chambers as shown in Figure 6: an entry 21, a sputtering chamber (vacuum chamber) 22, and an exit chamber 23. These chambers are separated by partitions. The transparent substrates 12 loaded on the pallet are conveyed in the direction of the arrow in the figure. The structure of the various chambers will be described in the pallet conveyance direction.

Page 31, line 14 to page 32, line 10, delete current paragraph and insert therefor:

B18

The entry chamber 21 is purged of air to create a vacuum on the inside. In the next chamber, the sputtering chamber 22, are formed shading films (light-shielding films, opaque films, non-transmitting films), such as chromium nitride (CrN) containing chromium and nitrogen (the first shading film (light-shielding films, opaque films, non-transmitting film) 13) and chromium carbide (CrC) containing chromium and carbon (the second shading film (light-shielding films, opaque films, non-transmitting film) 14), and anti-reflective film 15, such as chromium oxynitride (CrON) containing chromium, oxygen, and nitrogen. In other words, the film formation steps illustrated in Figure 3 are carried out. Although not shown in the figures, a plurality of chromium targets for forming the first and second shading films 13, 14 (light-shielding films, opaque films, non-transmitting films) and the anti-reflective film 15 are provided inside the sputtering chamber 22, and a plurality of valves for introducing atmosphere gas are provided near these targets. The last chamber, the exit chamber 23, is purged of air to create a vacuum on the inside, just as with the entry chamber 21.

Page 32, lines 11-17, delete current paragraph and insert therefor:

B19

When a photmask blank 31 is manufactured using the inline continuous sputtering apparatus described above, the first step is to introduce a pallet loaded with the quartz glass

B19 transparent substrates 12 into the entry chamber 21. The entry chamber 21 is then changed from the atmospheric pressure to a vacuum, after which the pallet is conveyed into the sputtering chamber 22.

Page 32, line 18 to page 33, line 18, delete current paragraph and insert therefor:

B20 In this sputtering chamber 22, the transparent substrates 12 loaded on the pallet are conveyed at a speed of 25 cm/min. At the first target, a mixed gas of Ar and N₂ (Ar: 80 vol%, N₂: 20vol%) is introduced through the first valve, and a chromium nitride (CrN) film formed as the first shading film (light-shielding film, opaque film, non-transmitting film) 13 (see Figure 3 (a)) in a thickness of 150 Å by reactive sputtering. At the second target, a mixes gas of Ar, CH₄, and He (Ar: 30 vol%, CH₄: 10 vol%, He: 60 vol%) is introduced through the second valve, and a chromium carbide (CrC) film filmed as the second shading film (light-shielding film, opaque film, non-transmitting film) 14 (see Figure 3 (b)) in a thickness of 600 Å by reactive sputtering. Then, at the third target, a mixed gas of Ar and NO (Ar: 80 vol%, NO: 20 vol%) is introduced through the third valve, and a chromium oxynitride (CrON) film is formed as the anti-reflective film 15 (see Figure 3 (c)) in a thickness of 250 Å by reactive sputtering. Three layers of film are thus formed continuously. The pressure inside the sputtering chamber 22 during the film formation was 0.3 Pa, the sputtering power at the target for the second shading film 14 (light-shielding film, opaque film, non-transmitting film) was 1650 W, and the deposition rate of the above-mentioned second shading film 14 (light-shielding film, opaque film, non-transmitting film) was 3.4 nm/sec.

Page 33, line 19 to page 34, line 4, delete current paragraph and insert therefor:

B21 After this, the pallet is moved into the vacuum-purged exit chamber 23. Once the sputtering chamber 22 and the exit chamber 23 have been completely separated by the partition, the exit chamber 23 is returned to atmospheric pressure. This yields a photomask

b21
blank 31. The pallets are continuously introduced, one after another, into the sputtering chamber 22 when the entry chamber 21 has reached the same state of vacuum as the sputtering chamber 22, so that at all times a plurality of pallets have been introduced into the sputtering chamber 22.

Page 34, lines 5-10, delete current paragraph and insert therefor:

b22
A commercially available apparatus was used to measure the optical characteristics of the photomask blank 31 produced in this manner, whereupon the optical density was 3.0 and the surface reflectance was 12% at a wavelength of 365 nm. Also, no particles were generated from the pallets and there were no film defects, meaning that film quality was good.

Page 34, line 13 to page 35, line 2, delete current paragraph and insert therefor:

b23
Figure 10 shows the results of analyzing the film composition of the photomask blank 31 thus obtained. Auger electron spectroscopy (AES) was used in the film composition analysis in Figure 10. Since helium content is not detected with Auger electron spectroscopy, the film composition analysis results in Figure 10 show the relative content when the total amount in which other elements (chromium, oxygen, nitrogen, carbon, silicon) were contained, excluding the helium content, was 100 at%. It can be seen from the measurement results obtained by Auger electron spectroscopy in Figure 10 that the composition varies continuously for the films that make up the photomask blank 31 formed by inline sputtering.

Page 35, lines 3-8, delete current paragraph and insert therefor:

b24
More specifically, in the anti-reflective film 15 and the second shading film 14 (light-shielding film, opaque film, non-transmitting film), the oxygen content continuously decreased and the carbon content continuously increases from the thin film surface side toward the transparent substrate 12 side, and nitrogen is contained in both of these films.

Page 36, lines 3-9, delete current paragraph and insert therefor:

b25
The nitrogen in the nitride film of the first shading film 13 (light-shielding film, opaque film, non-transmitting film) is contained in a relatively larger amount than the nitrogen contained in the anti-reflective film and the second shading film 14 (light-shielding film, opaque film, non-transmitting film), and the nitrogen content varies continuously.

Page 36, lines 10-25, delete current paragraph and insert therefor:

b26
The nitrogen in the first shading film 13 (light-shielding film, opaque film, non-transmitting film) is included to prevent film defects (black spots) in the pattern, as well as to improve adhesion to the transparent substrate. The etching rate can be raised by including nitrogen in a relatively larger amount than the nitrogen contained in the anti-reflective film 15 and the second shading film 14 (light-shielding film, opaque film, non-transmitting film), so film residue (black spots) left by etching can be prevented. The nitrogen content is 0 to 65 at%, and the amount should average 5 to 60 at% in the film. In addition to nitrogen, the first shading film 13 (light-shielding film, opaque film, non-transmitting film) may also contain small amounts of carbon and oxygen.

Page 37, lines 5-19, delete current paragraph and insert therefor:

b27
In order to better control these optical characteristics and the etching rate for obtaining the desired pattern shape, the photomask blank 31 of the present invention is structured such that in the anti-reflective film 15 and the second shading film 14 (light-shielding film, opaque film, non-transmitting film), the oxygen content continuously decreases and the carbon content continuously increases from the thin film surface side toward the transparent substrate 12 side, the nitrogen in the nitride film if the first shading film 13 (light-shielding film, opaque film, non-transmitting film) is contained in a relatively larger amount than the nitrogen contained in the anti-reflective film 15 and the second shading film 14 (light-shielding film, opaque film, non-transmitting film), and the nitrogen

b27
content varies continuously.

Page 37, lines 20-24, delete current paragraph and insert therefor:

b28
Also, just as in Example 1 above, the photomask blank 31 was analyzed by thermal desorption gas analyzer (TDS), and desorption of the mass number (m/e) = 4 (He) was observed just as above, confirming that helium (He) was contained in the film.

Page 38, lines 1-6, delete current paragraph and insert therefor:

b29
The change in flatness was measured by the same method as described above which confirmed that here was little change ($-0.75 \mu\text{m}$) and there was little film stress. The positional precision of the mask pattern was also extremely good in a photomask 32 produced by the same method as in Example 1.

Page 38, lines 7-10, delete current paragraph and insert therefor:

b30
Since the films whose composition varied continuously were formed by inline sputtering, there were no abrupt steps between the films in a cross section of the patterns of the photomask 32, and a smooth, vertical pattern was obtained.

Page 38, lines 11-23, delete current paragraph and insert therefor:

b31
When films were thus formed on a transparent substrate 12, the introduction of helium gas into the atmosphere gas in the formation of a chromium carbide film containing chromium and carbon in which the film stress exhibited tensile stress changes, and a chromium oxide film containing chromium and oxygen, and especially a thick chromium carbide film (CrC), allowed film stress to be suppressed and made it possible to obtain a film with no film stress even in the chromium oxynitride (CrON) film containing oxygen that was continuously formed over the chromium carbide film. Furthermore, the application of inline continuous sputtering allowed a photomask blank 31 with good film quality to be obtained while still permitting mass production.